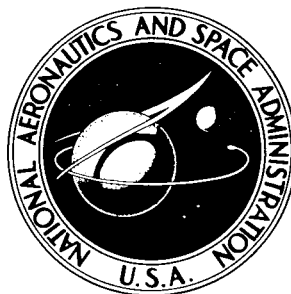


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DEPOSITION OF THIN FILMS BY ION PLATING ON SURFACES HAVING VARIOUS CONFIGURATIONS

*by Talivaldis Spalvins, John S. Przybyszewski,
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*Lewis Research Center
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SUMMARY

Thin gold films were ion plated on a variety of objects that have complex surface configurations. This process was performed on various substrate materials without rotating or moving the objects. Ion plating is unique in the respect that sputtering and ion deposition take place simultaneously. Because of the peculiar characteristics of the glow discharge (cathode dark space) during ion plating, the object can be uniformly plated on all surfaces. A strong bond is formed between the film and the substrate since the surface is continuously cleaned before and during the deposition process. This method may be of particular interest in the lubrication and friction field in depositing thin, soft metal films as lubricants.

A number of system components that have surfaces sliding against each other (bearings, gears, and seals) can be plated with a uniform metal film. In the corrosion field, ion-plated films may be employed to protect various complex surface configurations against corrosion or oxidation. The ion-plating method has an almost unlimited range of applications. It is particularly useful in plating surfaces with complex configurations and where the other conventional plating or deposition methods fail.

INTRODUCTION

The most commonly used coating techniques for metal films are electrodeposition, vacuum deposition by evaporation, and deposition by sputtering. The choice of the particular coating technique depends on a number of factors: the material to be deposited, geometry and surface configuration of the substrate material, film thickness and uniformity required, film structure, bonding properties or adhesion, and other factors not related to geometry (ref. 1).

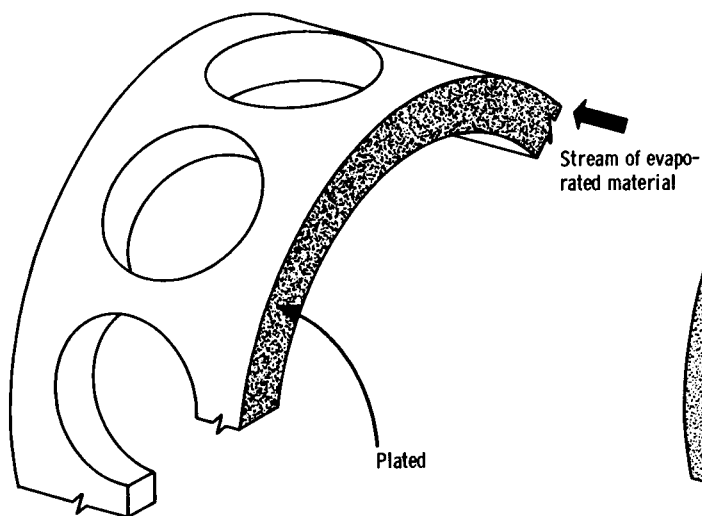
In electrodeposition, a uniform coating cannot be obtained on complex surfaces - especially those having edge effects as a result of potential differences. A higher accumulation of the deposited material will concentrate on the edges or the high points. In vacuum deposition and cathodic sputtering techniques, complex geometrical objects cannot be plated without rotating the object relative to the source. The evaporated atoms move only in straight lines; consequently, those surfaces of the complex shaped objects which are in direct line of travel to the stream of evaporated atoms are the only surfaces which are plated.

In addition to the three deposition methods discussed, there is a new method of coating objects with thin films that has recently been developed. This new method is known as ion plating. Ion plating is a highly versatile technique for depositing thin films on objects with complex configurations made from various materials that cannot be uniformly plated by other conventional techniques. The significant advantage of ion plating is that materials may be easily plated with a fairly uniform film in a single operation while keeping the object in a fixed position. Figure 1 compares the evaporation characteristics of the conventional vacuum-deposition methods with the ion-plating method.

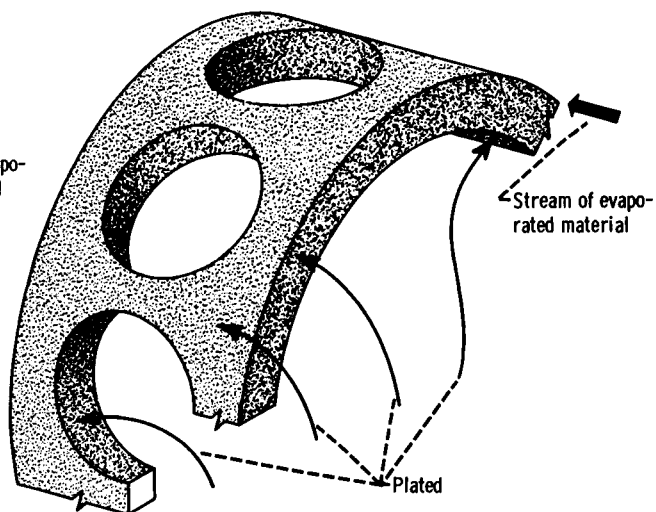
For many applications, thin, uniform, adherent films are needed. Ion plating may be of particular interest in the friction and lubrication field for plating system components which involve surfaces sliding on each other (bearings, seals, gears, etc.). Where solid film lubrication is required, such as in high temperature bearing applications, for example, ion plating can be used to deposit thin metallic films on the ball bearing component surfaces especially in the pockets of the cage. Another application would be plating of threaded bolts or shafts with a thin film to prevent galling. In the corrosion field, ion plating can protect various complex surfaces against corrosion or oxidation. In general, this method may be of significant value where regular vacuum-deposition methods fail to accomplish the purpose. The objective of this study was to develop a process by which uniform, adherent, thin films could be deposited on complex geometrical surfaces.

ION-PLATING PROCESS

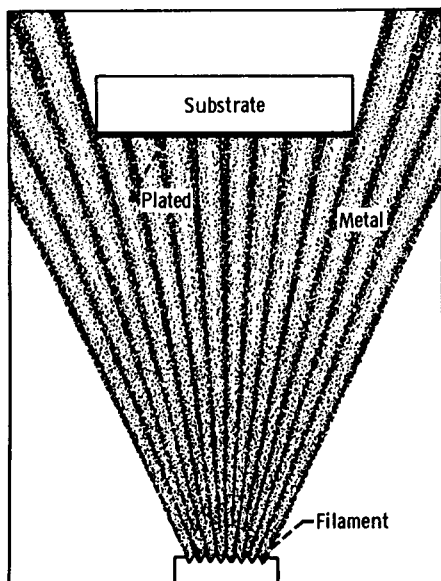
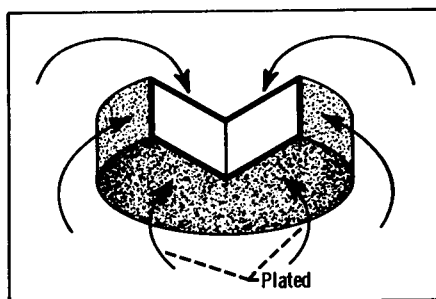
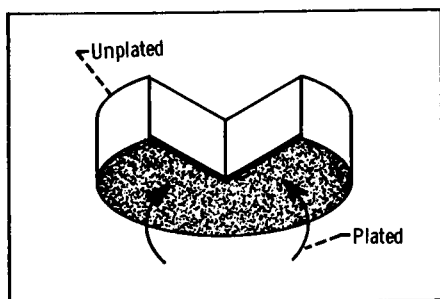
The ion-plating technique is a recent development that was first reported in the literature in 1963 (ref. 2). Many aspects and characteristics of this technique are still unknown. Basically, the process consists of sputtering and ion plating. A direct-current gas discharge is established between the cathode (object to be plated) and the anode (evaporant source) by admitting an inert gas (e. g. , Ar) into a previously evacuated system and applying a potential (3 to 5 kV) across the two electrodes. At low pressures



Cross section of partially plated complex-shape cage

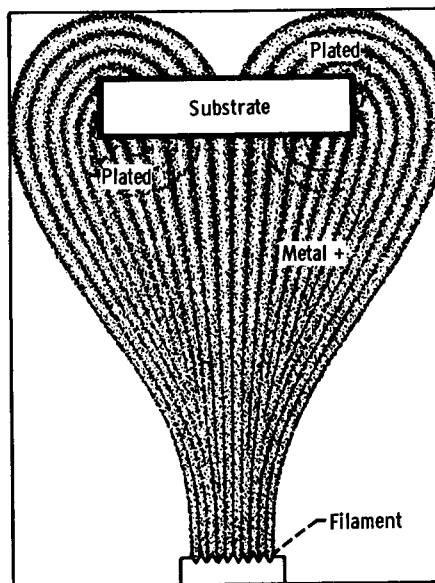


Cross section of completely plated complex-shape cage



Partially plated disk

(a) Conventional vacuum deposition.



Completely plated disk

(b) Ion plated.

Figure 1. - Comparison of conventional vacuum-deposition with ion-plating techniques.

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(15 to 40 μ Hg), a glow discharge is formed from the ionized inert gas (Ar). These positive argon ions (gaseous plasma) are accelerated and bombard a negatively charged target material, the cathode. This process is known as sputtering or cathodic bombardment, and is used to prepare the surface for metallic deposition.

Once the process described is established, the plating material is heated and evaporates into the positive glow region of the gas discharge. The evaporated atoms are ionized and accelerated toward the substrate with a high velocity, thus forming a film. Essentially, in ion plating there are two processes, sputtering and ion plating, taking place simultaneously, each of which has a cancelling or competing effect on the other. In order to obtain a film, it is important that the rate of deposition be higher than the rate of sputtering.

In ion plating, the object to be plated is the termination point for an electric field which exists between the evaporation source and the object. There is a difference of potential between any point on the object and the source. Once the evaporant is ionized in the argon glow discharge, the charged ions follow the electric lines of force to all points on the specimen surface if shielding effects are not present. As a result, it is possible to obtain a uniform film over the entire surface of complex configurations (threaded bolts, springs, rings, notched specimens, etc.). The fairly uniform distribution of the film over the entire surface of the material is apparently due to the fact that the

cathode dark space, which acts as the effective source of the evaporant, completely surrounds the object to be plated.

A strong bond is secured between the film and the substrate since the surface is continuously cleaned (by ion bombardment) before and during the deposition process. Also, the high energy metal ions penetrate the surface and establish an interface which is desirable for strong film bonding.

APPARATUS

The ion-plating apparatus shown in figure 2 consists basically of a vacuum chamber (bell jar), a fully floating direct-current high-voltage power supply (0 to 6 kV), a separate fully floating

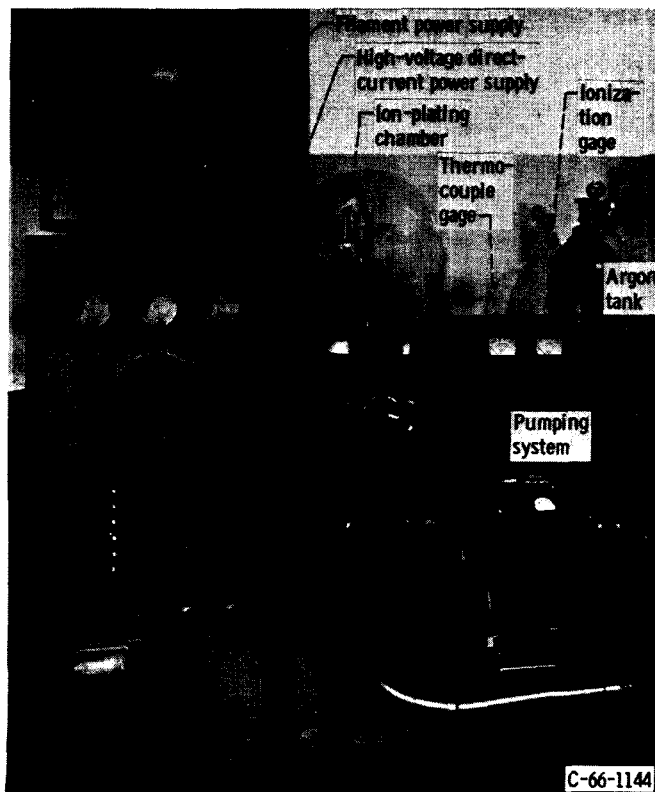


Figure 2. - Complete ion-plating system.

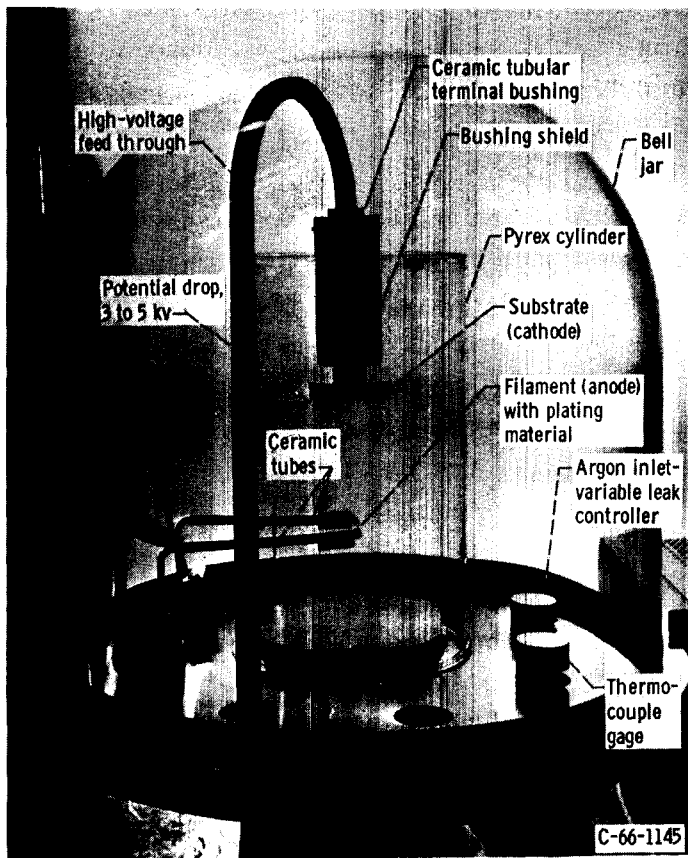


Figure 3. - Ion-plating chamber.

filament power supply and a tank of ultrapure argon. The pumping system of the vacuum chamber consists of a mechanical pump, an oil diffusion pump, and a liquid-nitrogen cold trap. The chamber was evacuated to a pressure of 10^{-6} to 10^{-7} millimeter of mercury. The vacuum chamber as shown in figure 3 consists of a Pyrex bell jar (18-in. diam by 18-in. height) which encloses the sputtering and plating components. The object to be plated is mounted on a tubular ceramic-insulated terminal bushing which is an integral part of the high-voltage feedthrough and connected to the negative terminal of the power supply (cathode). The terminal bushing is covered by a shield to prevent deposition of the plating material on the insulator and the feedthrough.

The filament (anode) is constructed

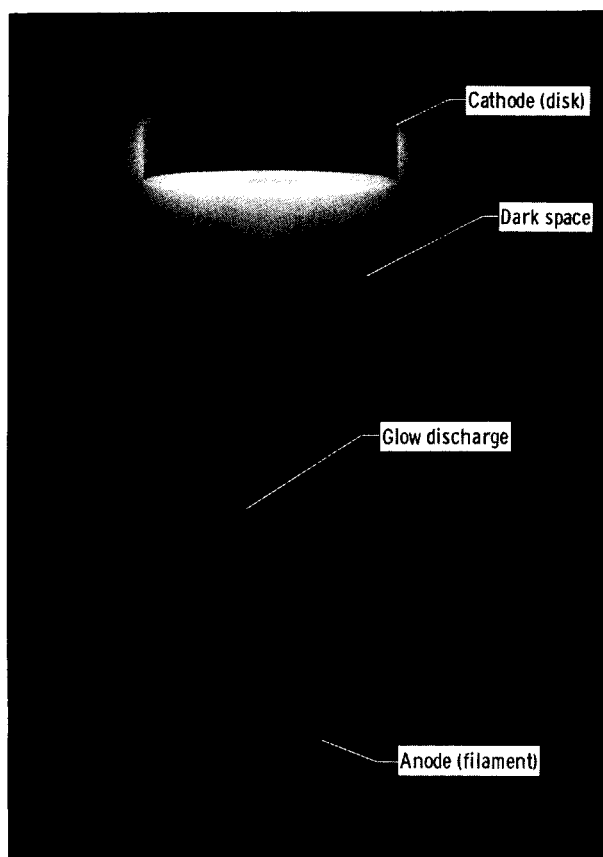
from two interwound 0.030-inch-diameter molybdenum wires about 2 inches in length. The evaporating material is a 0.020-inch-diameter gold wire of 99.999 percent purity. The gold wire is wound around the molybdenum filament. The filament holders are protected from sputtering by ceramic tubing. A 6-inch-diameter Pyrex cylinder encloses the electrodes and contains the glow discharge within a limited area. This cylinder also prevents sputtered and evaporated material from contaminating the whole chamber. Argon is admitted to the vacuum chamber through a variable leak-control valve. A thermocouple gage monitors the chamber pressure during the sputtering and plating operations.

PROCEDURE

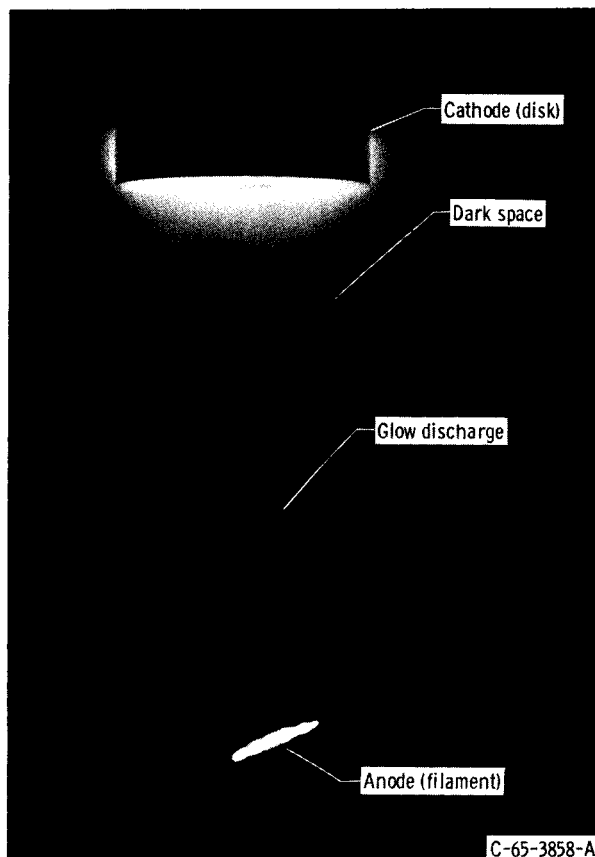
After mounting the substrate (cathode) and filament (anode), the chamber is evacuated to a pressure of 10^{-6} to 10^{-7} millimeter of mercury. This procedure rids the system of the bulk of the active gases which would tend to contaminate the sputtered surface and the freshly deposited film. After the system is evacuated, the chamber is

purged with pure argon through a variable leak valve. The purging operation was repeated several times. Finally, the system is evacuated, and argon is introduced at a controlled rate. A constant pressure is maintained in the chamber (within the range of 20 to 35 μ Hg.). Once a constant pressure is obtained, a potential of 3 to 5 kilowatts is gradually applied across the electrodes.

The potential across the electrodes ionizes the argon and forms a pinkish-violet plasma. The positive argon ions (Ar^+) impinge with high velocity on the cathode. These ions have sufficient energy to knock (sputter) atoms from the surface of the target material, thus cleaning the surface. The cleaning procedure is continued for 10 to 20 minutes; evidence of cleaning is noted by the accumulation of sputtered material on the walls of the inner cylinder. While the sputtering is in progress, the filament power supply is turned on. For the filament, described in the APPARATUS section, a current of 35 to 40 amperes is required. To heat the filament to the required temperature, the current is gradually increased until the temperature is high enough to melt the gold wire which then wets the molybdenum filament. When the filament is wetted, the evaporation rate of the plated material is proportional to the filament current. Figure 4 shows the



(a) Cleaning process.



(b) Plating process.

C-65-3858-A

Figure 4. - Glow discharge during ion plating.

actual glow discharge during ion plating; the cleaning process (sputtering) is shown in figure 4(a), and the ion plating is shown in figure 4(b).

In this investigation, the duration of evaporation was continued for about 20 seconds. The rate of evaporation was controlled by varying the filament current; increasing the current increased the rate of evaporation. The thermally evaporated gold atoms from the filament are injected into the argon plasma where they are ionized. In the cathode dark space the gold ions are accelerated towards the cathode. When the rate of evaporation is higher than the rate of sputtering, a film forms on the substrate. In order to avoid detrimental sputtering of the deposited film, the high-voltage direct current must be reduced before turning off the filament current and before the evaporant material is completely depleted.

CATHODE DARK SPACE CONSIDERATIONS

In sputtering and ion plating, a direct-current gas discharge is established between the cathode and anode. The volt-ampere characteristics of a gas discharge are presented in figure 5. Several specific regions can be distinguished, but the region of interest here is the abnormal glow discharge region, which is where ion plating is performed. In this region, the current is increased to such a value that the cathode is completely covered with the cathode glow. As the circuit current is further increased, the cathode current density increases and the voltage drop of the discharge also increases (refs. 3 and 4). When the pressure in the chamber is from 15 to 50 microns of mercury, a distinct dark zone surrounding the substrate (cathode) can be easily distinguished in the pinkish-violet plasma. The plasma is basically a region of ionized argon (Ar^+). This is the region of uniform light intensity, and there is little voltage drop across it. The dark

space can be expanded at the expense of the positive region. The significance of the cathode dark space is that, within this region, ions are sufficiently accelerated to produce secondary electrons on collision with the cathode. In this region, the ions are accelerated with the highest velocity toward the cathode. The most effective discharge therefore, is obtained when the edge of the dark space is in close proximity to the filament. When the dark space is as wide as possible, the most effective use of

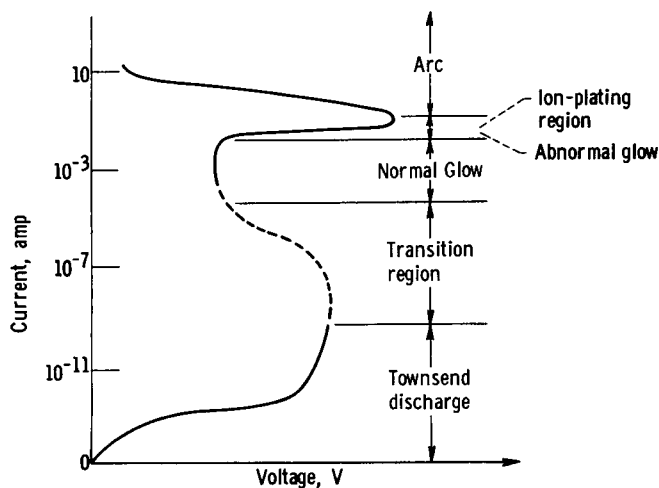


Figure 5. - Volt-ampere characteristics of gas discharge (ref. 5).

the evaporated material is obtained. The electrode spacing, the pressure, and the cathode dark space are all interrelated; therefore, if the anode to cathode distance is less than the width of the cathode dark space at a particular pressure, no current will flow. In this investigation the cathode spacing was 4 to 5 inches at a pressure of 25 to 30 microns of mercury, and the current density was about 0.3 to 0.8 milliamperes per square centimeter. If the cathode dark space is expanded to the point where it comes in contact with the anode, the discharge is extinguished. The dark space may be expanded or contracted either by decreasing or increasing the pressure. When the pressure is about 20 microns of mercury, the cathode dark space is several centimeters wide.

RESULTS AND DISCUSSION

The technique of ion plating was examined with the deposition of gold on various substrates. The disks shown in figure 1 were ion plated with gold, and the uniformity of the film was measured with an interference microscope. It was determined that, in this particular instance, the film thickness was about 1500 Å with a uniform distribution all over the disk. The thickness of the film was measured on the front, back, and sides of the disk. All measured values were in the 1300 to 1500 Å range.

Components of a ball bearing (fig. 6) were ion plated with a thin film of gold. It is of particular interest to note that the entire surface area of the cage, including the ball pockets (fig. 1(b)), was fairly uniformly plated with a thin film. This operation was accomplished without rotating or moving the cage. A new method is thus available whereby thin, uniform films used as lubricants can be applied in one operation and with a con-

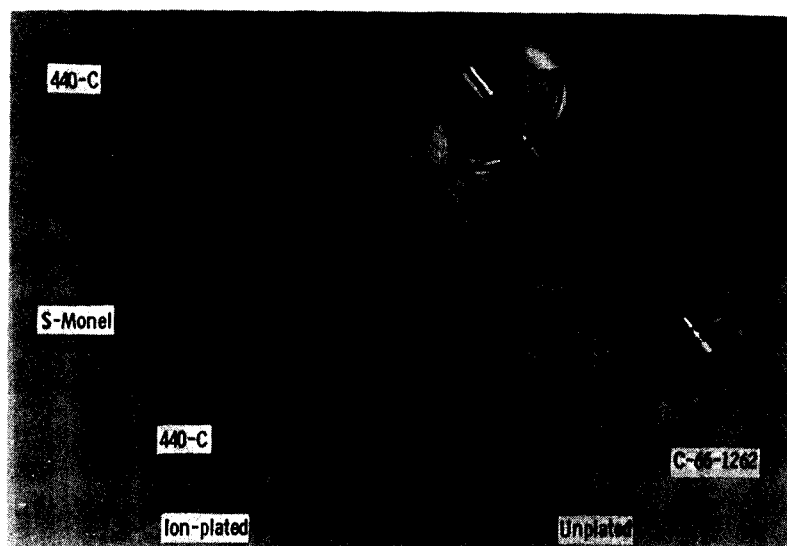


Figure 6. - Gold ion plated and unplated bearing assembly.

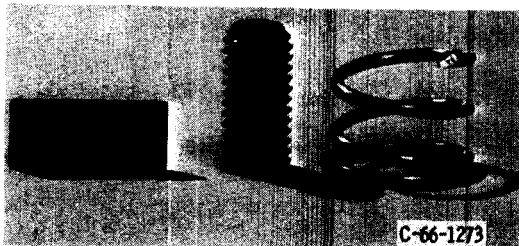


Figure 7. - Ion-plated complex stainless-steel surfaces.

trolled thickness. A number of complex surfaces were ion plated, and two of these are shown in figure 7.

Strong bonding (adhesion) was obtained between the film and substrate material. This determination was made by an adhesive tape test. This test, although qualitative, gives a good comparison between films with good and poor adhe-

sion to the substrate. The good bonding properties can be attributed to the fact that surface cleaning occurs while the film is deposited. Since the metal ions impinge on the surface with a high energy, they can penetrate several lattice spacings into the surface and form a compound.

It is also interesting to note that aluminum surfaces were discolored during the gold ion plating. A dark purple compound (believed to be Au Al_2) was formed. This discoloration appeared shortly after the gold evaporation was started; as the gold continued to evaporate, variations of color on the surface appeared before gold film, with the characteristic color of gold, completely covered the surface. This indicates the formation of an intermetallic compound between the substrate and the films. In this study, gold was selected as the plating material, but any metal can be used, depending on the particular film needs.

This method may be of significant importance in plating various complex surface configurations in one operation without rotating or moving the object. It is especially useful in depositing a continuous metal film on complex surfaces where other conventional deposition techniques fail.

SUMMARY OF RESULTS

The ion-plating method is of importance in thin-film deposition processes where the regular vacuum techniques fail. The following characteristics were observed:

1. Complex geometrical shapes with various surface configurations were plated in one operation with a uniform film without the need for rotation.
2. Clean substrates with strong bonding between the film and the substrate were achieved.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 26, 1966,
129-03-13-02-22.

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